Preparation and Crystal Structure of $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ (cp = η-C_5H_5) containing the New Binary Tungsten(IV) Fluoride Anion $[W_4F_{18}]^{2-}$ †

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The metallocene $[WCl_2(cp)_2]$ (cp = η-C_5H_5) was treated with WF_6 in sulfur dioxide solution yielding the ionic complex species $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ **1** and $[WCl_2(cp)_2]^{2+}[WF_6]^-{}_2$. Compound **1** was also obtained, in quantitative yield, from the reaction of elemental tungsten with two equivalents of $[WCl_2(cp)_2]$ and three equivalents of WF_6. It crystallizes in the orthorhombic space group *Pnma* (no. 62) with cell parameters a = 13.625(5), b = 11.225(3) and c = 22.350(3) Å. The crystal data were collected at 23 °C and the final refinement values are R = 0.0308 and R' = 0.0341. The thermodynamics of the oxidation of $[WCl_2(cp)_2]$ to give the tungsten(V) monocation in complex **1** are discussed on the basis of a Born–Haber cycle.

In our research group recently we have been interested in the oxidation of neutral metallocene(IV) derivatives to give d^0 cations. In this context we studied the reaction behaviour of AsF_5 towards the Group 5 and 6 metallocene species $[MCl_2(cp)_2]$ (M = V, Nb, Mo or W; cp = C_5H_5) [equations (1) and (2)].[1–4]

$$[MCl_2(cp)_2](M = V \text{ or } Nb) + \tfrac{3}{2}\,AsF_5 \longrightarrow [MCl_2(cp)_2]^+[AsF_6]^- + \tfrac{1}{2}\,AsF_3 \quad (1)$$

$$[MCl_2(cp)_2]\ (M = Mo \text{ or } W) + 3\,AsF_5 \longrightarrow [MCl_2(cp)_2]^{2+}[AsF_6]^-{}_2 + AsF_3 \quad (2)$$

The molecular structures of the d^0 monocationic species $[MCl_2(cp)_2]^+$ (M = V or Nb)[3,4] and of the d^0 dications $[MCl_2(cp)_2]^{2+}$ (M = Mo or W)[2] were elucidated by X-ray crystallography. The existence and stability of the structurally characterized bis(cyclopentadienyl) molybdenum d^1 complexes $[MoX_2(cp)_2]^+[PF_6]^-$ (X = Cl or Br)[5,6] led naturally to the attempted preparation of the tungsten analogues. Although the preparation of $[WX_2(cp)_2]^+$ cations (X = Cl or Br) has been reported in the literature[5,7] these species are relatively poorly characterized. Herein we report the preparation of a WF_6^- salt containing the $[WCl_2(cp)_2]^{2+}$ dication [NB the AsF_6^- salt was previously examined by X-ray crystallography[2]] and the preparation and crystal structure of $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$.

Table 1 Analytical data for compounds **1** and **2**

Compound	M	Analysis[a] (%) C	H	Cl
1[b]	1847.26	13.05 (13.00)	1.15 (1.10)	7.75 (7.70)
1[c]	1847.26	13.10 (13.00)	1.20 (1.10)	7.80 (7.70)
2[b]	980.63	12.30 (12.25)	1.00 (1.00)	7.20 (7.25)

[a] Required values given in parentheses. [b] Formed according to equation (3). [c] Formed according to equation (4).

Table 2 IR data* (cm^{-1})

$[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ **1**	$[WCl_2(cp)_2]^{2+}[WF_6]^-{}_2$ **2**	Assignment[9,10]
3118s	3100m	ν(CH)
1438s, 1430 (sh)	1425m	ω(CC)
1125w	Not observed	Δ(CCC)
868vs (br)	860s, 800s	γ(CH)
700m, 598vs (br)	570vs (br)	ν(WF)
345w, 295s	370m, 285s	ν(WCl)

* Substance as a powder between KBr plates (KBr reference used).

Results and Discussion

The metallocene, $[WCl_2(cp)_2]$, was treated with two equivalents of WF_6 [equation (3)] in sulfur dioxide at room temperature to

$$4\,[WCl_2(cp)_2] + 8\,WF_6 \longrightarrow \underset{\mathbf{1}}{[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}} + \underset{\mathbf{2}}{2\,[WCl_2(cp)_2]^{2+}[WF_6]^-{}_2} \quad (3)$$

yield ruby red $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ **1** and green $[WCl_2(cp)_2]^{2+}[WF_6]^-{}_2$ **2**, which are stable in sulfur dioxide solution and in the solid state at room temperature. They were readily separated from a black and insoluble by-product by filtration. Whereas complex **2** is soluble in liquid sulfur dioxide solution, pure and highly crystalline **1** crystallizes from the reaction mixture on standing for 24 h.

We were surprised to find that compound **1** had been formed in reaction (3). In fact WF_6 is usually reduced to give WF_6^- (W^V),[8] compound **2**, rather than the $[W_4F_{18}]^{2-}$ anion (W^{IV}). Subsequently compound **1** was prepared quantitatively according to equation (4) in liquid sulfur dioxide solution.

$$2[WCl_2(cp)_2] + 3\,WF_6 + W \xrightarrow{\text{ultrasound}} \mathbf{1} \quad (4)$$

Compounds **1** and **2** are sensitive towards air and moisture and are, due to qualitative measurements, paramagnetic, both in solution and in the solid state. Both compounds have been

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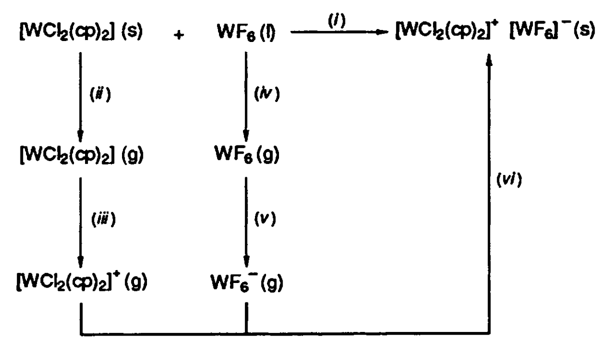
† *Supplementary data available:* Further details concerning the crystal structure determination may be obtained from Fachinformationszentrum Karlsruhe Gesellschaft für wissenschaftlich-technische Information, mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting reference CSD 56538.

Non-SI unit employed: cal = 4.184 J.

Table 3 Atomic positional parameters with estimated standard deviations (e.s.d.s) in parentheses for compound **1**

Atom	*x*	*y*	*z*
W(1)	−0.229 17(8)	$\frac{1}{4}$	0.359 31(5)
W(2)	0.964 82(9)	$\frac{1}{4}$	0.684 73(5)
W(3)	0.351 9(1)	$\frac{1}{4}$	0.550 11(5)
W(4)	0.146 10(8)	$\frac{1}{4}$	0.418 01(5)
W(5)	0.367 94(6)	0.432 93(6)	0.415 27(3)
Cl(1)	−0.108 0(4)	0.104 8(5)	0.338 5(3)
Cl(2)	0.849 0(7)	0.107 6(8)	0.716 9(4)
F(1)	0.096(1)	$\frac{1}{4}$	0.349 0(9)
F(2)	0.064 7(8)	0.135(1)	0.454 8(5)
F(3)	0.240 0(9)	0.372(1)	0.406 7(5)
F(4)	0.211(1)	$\frac{1}{4}$	0.506 2(7)
F(5)	0.287(1)	0.137(1)	0.598 8(5)
F(6)	0.375(1)	0.372(1)	0.493 6(5)
F(7)	0.461(2)	$\frac{1}{4}$	0.585(1)
F(8)	0.377 0(8)	0.445(1)	0.331 9(4)
F(9)	0.506 1(7)	0.451(1)	0.414 6(6)
F(10)	0.410(1)	$\frac{1}{4}$	0.395 8(6)
F(11)	0.338(1)	0.573(1)	0.429 9(6)
C(11)	−0.275(2)	0.178(3)	0.264 6(9)
C(12)	−0.353(2)	0.141(4)	0.307(1)
C(13)	−0.391(3)	$\frac{1}{4}$	0.322(2)
C(21)	−0.334(2)	$\frac{1}{4}$	0.441(1)
C(22)	−0.276(2)	0.150(2)	0.444(1)
C(23)	−0.178(2)	0.186(4)	0.454 0(9)
C(31)	0.866(3)	$\frac{1}{4}$	0.600(2)
C(32)	0.935(3)	0.148(2)	0.596(1)
C(33)	1.029(2)	0.189(2)	0.593(1)
C(41)	1.022(4)	$\frac{1}{4}$	0.782(1)
C(42)	1.065(2)	0.148(3)	0.749(1)
C(43)	1.127(2)	0.184(2)	0.707(1)



Scheme 1 Energy cycle to estimate the heat of reaction (ΔH^0) according to equation (5). (*i*) $\Delta H^\circ = -1$ kcal mol^{-1}. (*ii*) $\Delta H_{sub}^\circ = 23$ kcal mol^{-1}, taken to be equal to $\Delta H_{sub}^\circ\{[ZrCl_2(cp)_2]\}$.[1] (*iii*) Ionization energy (E_i) = E_i(W) − 1 = 6.98 eV (≈161 kcal mol^{-1}), calibrated on $E_i\{[MoCl_2(cp)_2]\} = E_i(Mo) - 1$ eV.[11] (*iv*) $\Delta H_{vap} = 6$ kcal mol^{-1}.[10] (*v*) Electron affinity (E_{ea}) = −85 kcal mol^{-1}.[10] (*vi*) Crystal lattice energy (U) = −106 kcal mol^{-1}, calculated from the molecular volume (V_M/Å^3), using the linear relationship: $U = 556.3\ (V_M)^{-0.33} + 26.3$,[12,13] where $V_M(WF_6^-) = 109$ Å^3 (ref. 1) and $V_M\{[WCl_2(cp)_2]^+\}$ was taken to be equal to $V_M\{[MoCl_2(cp)_2]^+\} = 230$ Å^3 (ref. 6) [covalent radii of Mo and W *ca.* 1.30 Å[14]]

characterized by elemental analyses (Table 1) and IR spectroscopy (Table 2).

Using a simple Born–Haber energy cycle (Scheme 1), we estimated the heat of reaction (5) [ΔH° (5)], the oxidation of

$$[WCl_2(cp)_2] + WF_6 \longrightarrow [WCl_2(cp)_2]^+[WF_6]^- \quad (5)$$

$[W^{IV}Cl_2(cp)_2]$ with WF_6 to give a salt containing the $[W^VCl_2(cp)_2]^+$ cation. Although the value for the ionization energy of $[WCl_2(cp)_2]$ might be slightly overestimated, the estimated value of ΔH° (5), −1 kcal mol^{-1}, clearly shows that the oxidation of $[WCl_2(cp)_2]$ by WF_6 is close to the borderline between a thermodynamically favoured and unfavoured reaction. The experimentally observed formation of the dication $[W^{VI}Cl_2(cp)_2]^{2+}$ can be explained by the significantly greater crystal lattice energy for **2** compared with **1** [U(**2**) ⩾ 2 U(**1**); *cf.* ref. 15] although the ionization energy of $[WCl_2(cp)_2]^+$ is larger than that of $[WCl_2(cp)_2]$.

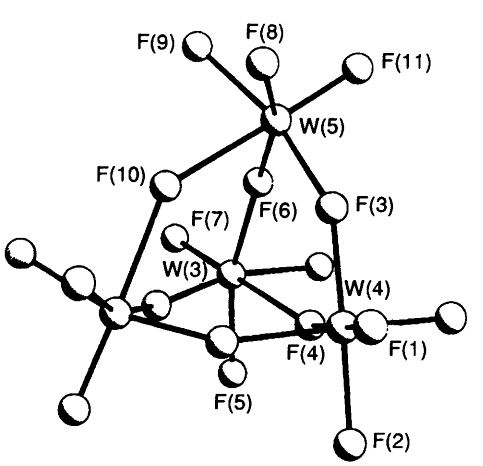


Fig. 1 PLUTO[16] representation of the $[W_4F_{18}]^{2-}$ anion in compound **1**

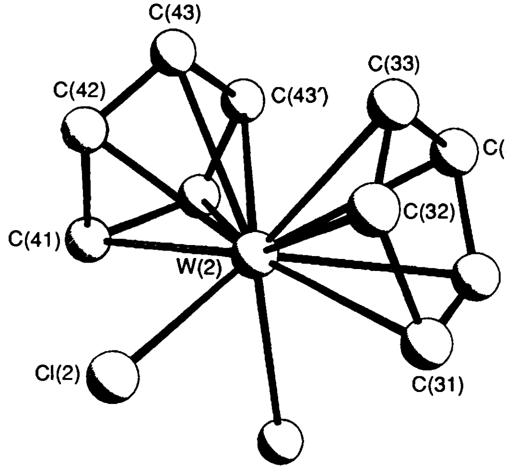


Fig. 2 PLUTO[16] representation of the $[W(cp)_2Cl_2]^+$ cation in compound **1**

Crystal Structure of $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ **1**.—The structure of compound **1** has been resolved and refined successfully with no unusual features. Since the space group is centrosymmetric, the crystals are either racemic, or the molecule does not contain an asymmetric centre. Atomic parameters are given in Table 3. Interatomic distances and bond angles are given in Table 4. Fig. 1 shows the cluster-like $[W_2F_{18}]^{2-}$ anion in **1** and Fig. 2 the $[WCl_2(cp)_2]^+$ cation. There are no significant cation–anion interactions.

The structural parameters of the $[WCl_2(cp)_2]^+$ cation in **1** agree well with those observed in the isostructural $[MoCl_2(cp)_2]^+$ ion. The average W–Cl bond length in compound **1** is 2.38 Å.[1,6] This is consistent with the essentially identical covalent radii of Mo and W (1.30 Å).[14] Therefore the average Cl–M–Cl (M = Mo or W) bond angle in **1** (86.3°) is very similar to the Cl–M–Cl angle in $[MoCl_2(cp)_2]^+$ (87.9°),[1,6] the slightly larger angle in the molybdenum species reflecting the higher effective nuclear charge in the cationic $[MoCl_2(cp)_2]^+$ compared with $[WCl_2(cp)_2]^+$ (*cf.* MoF_6 is a stronger oxidizer than WF_6).[17] The novel cluster-like $[W_4F_{18}]^{2-}$ anion contains a regular W_4 tetrahedron skeleton in which all six W–W edges

Table 4 Interatomic distances (Å) and bond angles (°) with e.s.d.s in the least significant figure in parentheses

W(1)–Cl(1)	2.366(5)	W(2)–C(33)	2.34(2)	W(4)–F(3)	1.89(1)	C(12)–C(13)	1.37(4)
W(1)–C(11)	2.35(2)	W(2)–C(41)	2.31(3)	W(4)–F(4)	2.16(2)	C(21)–C(22)	1.37(3)
W(1)–C(12)	2.39(3)	W(2)–C(42)	2.29(3)	W(5)–F(3)	1.88(1)	C(22)–C(23)	1.41(4)
W(1)–C(13)	2.35(4)	W(2)–C(43)	2.38(2)	W(5)–F(6)	1.88(1)	C(23)–C(23′)	1.44(9)
W(1)–C(21)	2.31(3)	W(3)–F(4)	2.16(1)	W(5)–F(8)	1.87(1)	C(31)–C(32)	1.48(4)
W(1)–C(22)	2.29(2)	W(3)–F(5)	1.89(1)	W(5)–F(9)	1.89(1)	C(32)–C(33)	1.36(4)
W(1)–C(23)	2.34(2)	W(3)–F(6)	1.89(1)	W(5)–F(10)	2.174(5)	C(33)–C(33′)	1.38(6)
W(2)–Cl(2)	2.358(7)	W(3)–F(7)	1.68(2)	W(5)–F(11)	1.66(1)	C(41)–C(42)	1.48(4)
W(2)–C(31)	2.33(4)	W(4)–F(1)	1.69(2)	C(11)–C(11′)	1.63(6)	C(42)–C(43)	1.32(3)
W(2)–C(32)	2.33(2)	W(4)–F(2)	1.89(1)	C(11)–C(12)	1.47(4)	C(43)–C(43′)	1.48(5)
Cl(1)–W(1)–Cl(1)	87.1(3)	Cl(2)–W(2)–Cl(2′)	85.4(5)	C(43)–W(2)–C(43′)	36(1)	W(3)–F(4)–W(4)	141.1(7)
Cl(1)–W(1)–C(11)	76.7(6)	Cl(2)–W(2)–C(31)	82.0(8)	F(4)–W(3)–F(5)	81.0(5)	W(3)–F(6)–W(5)	151.5(7)
Cl(1)–W(1)–C(11′)	104.3(8)	Cl(2)–W(2)–C(32)	79.2(7)	F(4)–W(3)–F(6)	81.0(5)	W(5)–F(10)–W(5)	141.6(7)
Cl(1)–W(1)–C(12)	92.5(8)	Cl(2)–W(2)–C(32′)	118.4(9)	F(4)–W(3)–F(7)	179.2(9)	W(1)–C(11)–C(11′)	69.8(7)
Cl(1)–W(1)–C(12′)	138.3(9)	Cl(2)–W(2)–C(33)	108.6(8)	F(5)–W(3)–F(5′)	84.0(8)	W(1)–C(11)–C(12)	73(1)
Cl(1)–W(1)–C(13)	125.7(5)	Cl(2)–W(2)–C(33′)	135.9(7)	F(5)–W(3)–F(6)	161.4(6)	C(11′)–C(11)–C(12)	106(2)
Cl(1)–W(1)–C(21)	125.8(5)	Cl(2)–W(2)–C(41)	86(1)	F(5)–W(3)–F(6′)	88.8(5)	W(1)–C(12)–C(11)	71(1)
Cl(1)–W(1)–C(22)	91.1(8)	Cl(2)–W(2)–C(42)	82.6(7)	F(5)–W(3)–F(7)	98.4(7)	W(1)–C(12)–C(13)	72(2)
Cl(1)–W(1)–C(22′)	133.8(7)	Cl(2)–W(2)–C(42′)	123.2(8)	F(6)–W(3)–F(6′)	92.8(7)	C(11)–C(12)–C(13)	101(4)
Cl(1)–W(1)–C(23)	76.0(8)	Cl(2)–W(2)–C(43)	110.2(7)	F(6)–W(3)–F(7)	99.6(7)	W(1)–C(13)–C(12)	75(2)
Cl(1)–W(1)–C(23′)	100(1)	Cl(2)–W(2)–C(43′)	140.2(6)	F(1)–W(4)–F(2)	99.2(6)	C(12)–C(13)–C(12′)	126(5)
C(11)–W(1)–C(11′)	40(1)	C(31)–W(2)–C(32)	37.1(9)	F(1)–W(4)–F(3)	98.7(6)	W(1)–C(21)–C(22)	72(2)
C(11)–W(1)–C(12′)	36(1)	C(31)–W(2)–C(33)	60(1)	F(1)–W(4)–F(4)	179.8(8)	C(22)–C(21)–C(22′)	109(3)
C(11)–W(1)–C(12)	63(1)	C(31)–W(2)–C(41)	164(2)	F(2)–W(4)–F(2′)	85.9(7)	W(1)–C(22)–C(21)	74(2)
C(11)–W(1)–C(13)	56(1)	C(31)–W(2)–C(42)	149.1(8)	F(2)–W(4)–F(3)	161.7(5)	W(1)–C(22)–C(23)	74(1)
C(11)–W(1)–C(21)	123(1)	C(31)–W(2)–C(43)	135(1)	F(2)–W(4)–F(3′)	87.8(5)	C(21)–C(22)–C(23)	109(3)
C(11)–W(1)–C(22)	120(1)	C(32)–W(2)–C(32′)	59(1)	F(2)–W(4)–F(4)	80.9(4)	W(1)–C(23)–C(22)	70(1)
C(11)–W(1)–C(22′)	147(1)	C(32)–W(2)–C(33)	33.9(9)	F(3)–W(4)–F(3′)	92.8(7)	W(1)–C(23′)–C(23)	72(1)
C(11)–W(1)–C(23)	142(1)	C(32)–W(2)–C(33′)	57.2(9)	F(3)–W(4)–F(4)	81.2(4)	C(22)–C(23)–C(23′)	106(2)
C(11)–W(1)–C(23′)	177(1)	C(32)–W(2)–C(41)	149.7(8)	F(3)–W(5)–F(6)	90.4(5)	W(2)–C(31)–C(32)	71(2)
C(12)–W(1)–C(12′)	61(2)	C(32)–W(2)–C(42)	113(1)	F(3)–W(5)–F(8)	89.2(5)	C(32)–C(31)–C(32)	100(3)
C(12)–W(1)–C(13)	33.5(8)	C(32)–W(2)–C(42′)	152(1)	F(3)–W(5)–F(9)	163.6(5)	W(2)–C(32)–C(31)	71(2)
C(12)–W(1)–C(21)	87(1)	C(32)–W(2)–C(43)	101(1)	F(3)–W(5)–F(10)	83.0(5)	W(2)–C(32)–C(33)	73(1)
C(12)–W(1)–C(22)	88(1)	C(32)–W(2)–C(43′)	119(1)	F(3)–W(5)–F(11)	97.8(6)	C(31)–C(32)–C(33)	110(2)
C(12)–W(1)–C(22′)	117(1)	C(33)–W(2)–C(33′)	34(1)	F(6)–W(5)–F(8)	161.4(5)	W(2)–C(33)–C(32)	73(1)
C(12)–W(1)–C(23)	120(1)	C(33)–W(2)–C(41)	135(1)	F(6)–W(5)–F(9)	89.9(5)	W(2)–C(33)–C(33′)	72.9(7)
C(12)–W(1)–C(23′)	144(1)	C(33)–W(2)–C(42)	100(1)	F(6)–W(5)–F(10)	80.1(5)	C(32)–C(33)–C(33′)	109(2)
C(13)–W(1)–C(21)	73(1)	C(33)–W(2)–C(42′)	118(1)	F(6)–W(5)–F(11)	100.1(6)	W(2)–C(41)–C(42)	71(1)
C(13)–W(1)–C(22)	92(1)	C(33)–W(2)–C(43)	75.2(9)	F(8)–W(5)–F(9)	85.3(5)	C(42)–C(41)–C(42′)	101(3)
C(13)–W(1)–C(23)	127(1)	C(33)–W(2)–C(43′)	86(1)	F(8)–W(5)–F(10)	81.4(5)	W(2)–C(42)–C(41)	72(2)
C(21)–W(1)–C(22)	34.6(8)	C(41)–W(2)–C(42)	38(1)	F(8)–W(5)–F(11)	98.4(6)	W(2)–C(42)–C(43)	77(2)
C(21)–W(1)–C(23)	58(1)	C(41)–W(2)–C(43)	59(1)	F(9)–W(5)–F(10)	80.9(5)	C(41)–C(42)–C(43)	112(3)
C(22)–W(1)–C(22′)	58(1)	C(42)–W(2)–C(42′)	60(1)	F(9)–W(5)–F(11)	98.2(5)	W(2)–C(43)–C(42)	70(2)
C(22)–W(1)–C(23)	35(1)	C(42)–W(2)–C(43)	32.8(8)	F(10)–W(5)–F(11)	179.1(6)	W(2)–C(43′)–C(43)	71.9(6)
C(22)–W(1)–C(23′)	59(1)	C(42)–W(2)–C(43′)	58.0(8)	W(4)–F(3)–W(5)	151.1(7)	C(42)–C(43)–C(43′)	108(2)
C(23)–W(1)–C(23′)	36(2)						

are bridged by a two-co-ordinated F atom. Additionally there are three terminal F atoms co-ordinated to each tungsten atom. The terminal W–F bond distances range from 1.66 [W(5)–F(11)] to 1.89 Å [W(5)–F(9)], whereas the bridging W–F bond lengths are longer on average and lie between 1.88 [W(5)–F(3)] and 2.17 Å [W(5)–F(10)]. Therefore the terminal W–F bond distances are slightly shorter than the sum of the covalent radii of W and F (1.30 + 0.72 = 2.02 Å)[14] whereas the bridging W–F bond distances indicate an expected bond order of less than one. These dimensions of the tetranuclear anionic species fit well with the general pattern of previously described halogenotungsten anions.[18]

Experimental

The reactions were carried out in glass vessels fitted with poly(tetrafluoroethylene) valves. All manipulations were carried out in an inert-gas atmosphere (N_2, dry-box). Gaseous WF_6 was added volumetrically using a calibrated Monel vacuum line.

The metallocene, $[W(cp)_2Cl_2]$, was prepared as described in the literature[19] and WF_6 (Air Products) and SO_2 (Messer Griesheim, stored over CaH_2) were purified by distillation. IR spectra were obtained using a Perkin-Elmer 580 B instrument. Microanalyses were performed either by the Technische Universität Berlin service or by the Analytische Laboratorien Engelskirchen.

Reaction of $[WCl_2(cp)_2]$ *with Two Equivalents of* WF_6.—At −196 °C WF_6 (0.85 g, 2.86 mmol) was condensed onto a frozen solution (10 cm^3) of $[WCl_2(cp)_2]$ (0.55 g, 1.43 mmol) in SO_2. The reaction mixture was warmed to room temperature and stirred for 5 min. After filtration (D4 frit) sulfur dioxide and all volatile species (*e.g.* traces of WF_6) were removed. The crude product was again dissolved in SO_2 (10 cm^3). Keeping this solution over a period of 24 h at room temperature yielded compound **1** as ruby red crystals [0.41 g, 62% according to equation (3)], which were suitable for an X-ray diffraction study. The remaining solution was then concentrated to 5 cm^3, filtered and the SO_2 was removed yielding compound **2** as a green solid [0.43 g, 61% according to equation (3)]. Analytical and IR data for **2** compare with those reported[2] for $[WCl_2(cp)_2]^{2+}[AsF_6]^-{}_2$.

Synthesis of $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ **1**.—At −196 °C WF_6 (0.45 g, 1.52 mmol) was condensed onto a frozen mixture (10 cm^3) of $[WCl_2(cp)_2]$ (0.39 g, 1.01 mmol) and activated W (0.09 g, 0.51 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min in an ultrasonic bath and was then allowed to react for 12 h. After filtration sulfur dioxide was removed yielding compound **1** as a ruby red solid (0.87 g, 94%). The analytical and IR data were consistent with those obtained from the first preparation.

X-Ray Crystal Structure Determination of $[WCl_2(cp)_2]^+{}_2[W_4F_{18}]^{2-}$ **1**.—Ruby red crystals were obtained from a solution of **1** in SO_2 at room temperature (see above).

Crystal data. $C_{20}H_{20}Cl_4F_{18}W_6$, $M = 1847.26$, orthorhombic, space group *Pnma* (no. 62), $a = 13.625(5)$, $b = 11.225(3)$, $c = 22.350(3)$ Å, $U = 3418(2)$ Å^3, $Z = 8$, $D_c = 3.589$ g cm^{-3}, $F(000) = 3256$, μ(Mo-Kα) = 15.01 cm^{-1}. Ruby red crystals. Crystal dimensions 0.50 × 0.50 × 0.50 mm (mounted in a glass capillary), λ(Mo-Kα) = 0.710 69 Å.

Data collection and processing. Rigaku diffractometer (AFC5R), ω–2θ scan mode ($2\theta_{max} = 60°$), $T = 23 \pm 1$ °C, graphite-monochromated Mo-Kα radiation; 4363 unique reflections up to the $2\theta = 60°$ measured, 1808 with $I_{net} \geqslant 3\sigma(I_{net})$ used for calculations. The linear absorption coefficient for Mo-Kα is 209.8 cm^{-1}. An empirical absorption correction, using the program DIFABS,[20] was applied, which resulted in absorption coefficients 0.831–1.105. The data were corrected for Lorentz and polarization effects.

Structure analysis and refinement. The structure was solved by direct methods[21] which revealed the positions of all non-hydrogen atoms. These atoms were refined anisotropically. The final cycle of the full-matrix least-squares refinement[21] was based on 1808 observed reflections $[I \geqslant 3\sigma(I)]$ and 235 variable parameters, and converged (largest parameter shift was 0.05 times its e.s.d.) with unweighted and weighted agreement factors of $R = 0.0308$ and $R' = 0.0341$ where $w = 1/\sigma^2(F)$. The standard deviation of an observation of unit weight was 2.054. The weighting scheme was based on counting statistics and included a factor ($p = 0.01$) to downweight the intense reflections. Plots of $w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, the reflection order in the data collection, sin θ/λ, and various classes of indices showed no unusual trends. A correction for secondary extinction was not applied. The maximum and minimum peaks in the final Fourier difference map corresponded to 1.04 and −1.12 e Å^{-3}, respectively.

Neutral atom scattering factors for the non-hydrogen atoms were taken from ref. 22 and the scattering factors for the hydrogen atoms from ref. 23. Anomalous dispersion effects were included in F_{calc};[24] the values for f' and f'' were from ref. 22. All calculations were performed using the TEXSAN[25] crystallographic software package.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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